Issued September 20, 1912.

U. S. DEPARTMENT OF AGRICULTURE,

FOREST SERVICE—BULLETIN 110.

HENRY S. GRAVES, Forester.

FOREST PRODUCTS LABORATORY SERIES.

THE SPECIFIC HEAT OF WOOD.

BY

FREDERICK DUNLAP,

Forest Assistant, Forest Service.

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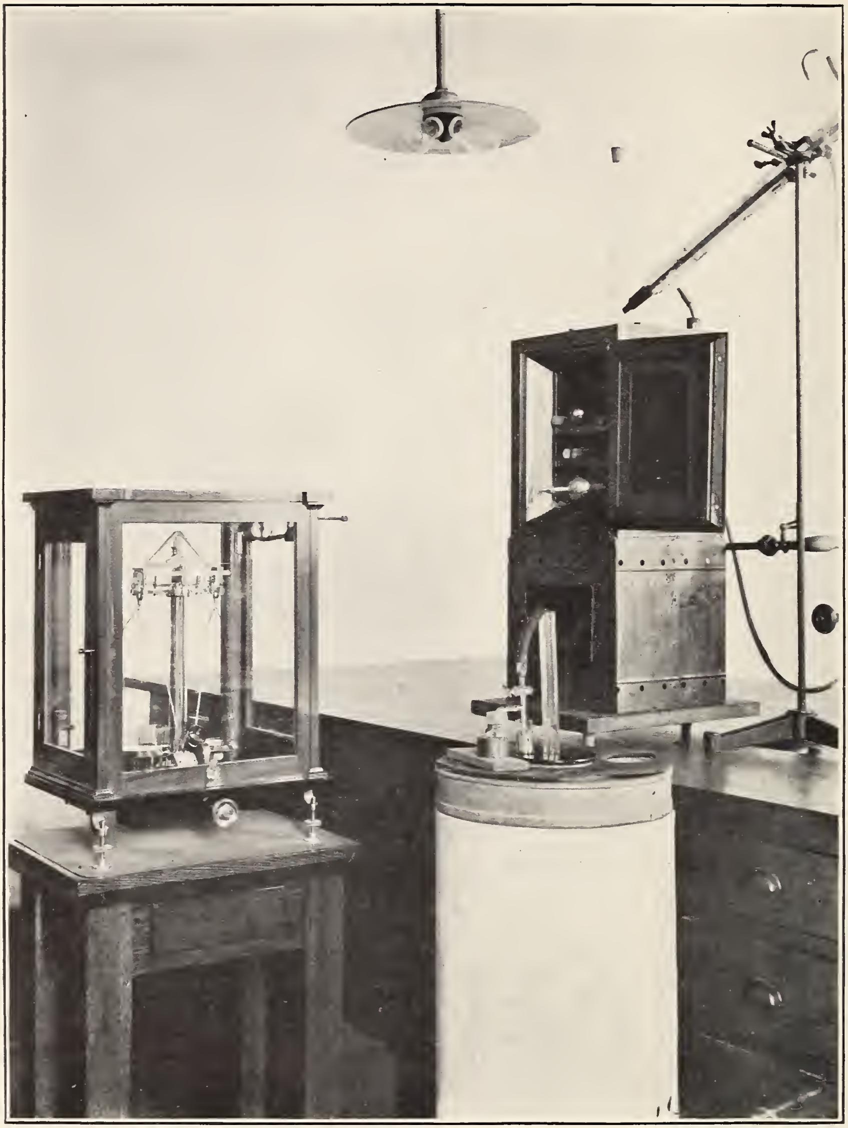

THE BALANCE, THE OVEN, AND THE UPPER PORTION OF THE CALORIMETER.

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LETTER OF TRANSMITTAL.

UNITED STATES DEPARTMENT OF AGRICULTURE,
FOREST SERVICE,
Washington, D. C., March 21, 1912.

SIR: I have the honor to transmit herewith a manuscript entitled "The Specific Heat of Wood," by Frederick Dunlap, Forest Assistant, and to recommend its publication as Bulletin 110 of the Forest Service.

Respectfully,

HENRY S. GRAVES,
Forester.

Hon. JAMES WILSON,
Secretary of Agriculture.

CONTENTS.

ILLUSTRATIONS.

PLATE.

TEXT FIGURES.

THE SPECIFIC HEAT OF WOOD.

IMPORTANCE OF DETERMINING THE SPECIFIC HEAT OF WOOD.

The specific heat of wood—that is, the heat capacity of a given weight of wood compared with the heat capacity of the same weight of water—is one of the fundamental physical properties which indicate its intrinsic nature and ultimate structure. The need for reliable knowledge of this property was first revealed by a study of dry-kiln operations. Different operators use different methods in drying the same material for the same purpose; and, although their methods differ only in detail, their conceptions of the manner in which drying takes place differ enormously. In spite of the high grade of intelligence and engineering skill devoted to the operation of the larger kilns, the results are in no case entirely satisfactory. The cause is the lack of familiarity with the minute structure and physical properties of wood. In fact, there are no reliable values for those physical properties which control the transfer of heat[1] or water through wood. Knowledge of the specific heat of wood is necessary, however, not only in dry-kiln operation, but also in solving certain problems of the preservative impregnation of wood, the distillation of wood, and of all processes in which wood is subjected to a change of temperature. Though this study aimed solely to secure reliable values for specific heat,[1] it is hoped that it may also direct attention to the study of the other fundamental physical properties, so that eventually a basis may be secured for the formulation of a rational theory of the nature and ultimate structure of wood and of its action under different treatments. While the results are of practical service in commercial practice, they are even more useful in laboratory experiments.

APPARATUS AND METHODS.

The specific heat was determined by measuring in a calorimeter the quantity of heat given off by small cylinders of oven-dry wood in falling from a temperature slightly above that of boiling water to that of melting ice. The result in calories, divided by the difference

[1] Prof. William Kent, in "The Mechanical Engineer's Pocketbook" (8th edition, 1910, p. 536), gives the specific heats of four species of wood, the values ranging from 0.467 to 0.650. Prof. Kent does not cite the source of these figures, but they appear to rest on determinations made by J. R. Mayer, of Heilbronn, a contemporary of Joule. Cf. Péclet, E. Traité de la Chaleur, 4th edition, 1878, Vol. I, p. 606.

38170°—Bull. 110—12——2

between the initial and final temperatures of the wood in degrees centigrade, and by its weight in grams, gives the mean specific heat of the wood through the range of temperature involved.

THE OVEN.

A copper drying oven, liquid jacketed, was used to bring the wood to the oven-dry condition and also to warm it before its introduction into the calorimeter. The oven was heated by gas. The jacket was filled with a mixture of water and glycerine, in about the proportion of 3 to 5, by volume. This mixture, when boiling, gave a temperature inside the oven from 5° to 10° above the boiling point of water. A reflux condenser maintained the constancy of the mixture in the jacket. The oven is shown in Plate I (frontispiece).

The temperature inside the oven was determined by means of an ordinary mercury-in-glass thermometer inserted through the top of the oven, with its bulb free in the air, near the center of the oven. This thermometer was calibrated in the oven against a carefully calibrated thermometer of the same type, and was read to twentieths of a degree centigrade.

THE CALORIMETER.

Bunsen's ice calorimeter,[1] in a slightly modified form, was used for measuring heat. The chief advantage of this calorimeter is that no radiation correction is necessary, because the introduction of heat is not indicated by a rise in temperature. This feature is particularly advantageous, since wood cools slowly.

The ice calorimeter depends for its indications upon the difference between the specific volumes of ice and water at the freezing point. It consists essentially of a mercury-sealed reservoir of water. After the water has been partially frozen the calorimeter is packed in melting ice, which prevents either freezing or thawing. The introduction of a hot body supplies heat and melts a portion of the ice, so that the amount of ice in the reservoir is diminished and the amount of water is increased while both remain at the melting point of ice. The heat produces no rise in temperature, but is entirely consumed in melting a portion of the ice. Since ice occupies 9 per cent more volume than does the water from which it is frozen, the melting of a portion of the ice in the reservoir causes the contents to contract. The measurement of this contraction indicates the amount of heat introduced.

The calorimeter used is shown in section in figure 1. The long glass tube at the axis is provided for the reception of the heated wood; its lower end, A, projects into the cylindrical jacket B. The upper end of this jacket is sealed to the tube, and the lower end opens into

[1] Bunsen, R. Calorimetrische Untersuchungen. Pogg. Ann. CXLI, pp. 1-31, 1870.

a narrow tube, C, which drops, curves upon itself, and rises past the side of the jacket to near the top of the central tube. The upper end of the tube C is enlarged into the cup D. These three parts, A, B, and C (with D), are the essential constituents of Bunsen's calorimeter. The body (B) of the instrument is filled with water above and mercury below, the mercury filling also the arm at the side and rising into the cup at the end of the arm. (See fig. 1.)

After partially freezing the water Bunsen packed this instrument in clean snow and attached a capillary glass tube to the top of C through a cork stopper. Then he noted, by the recession of the mercury meniscus in the capillary tube, the change in volume produced by the introduction of heat into the tube A. Bunsen's instrument was much smaller than the one used in these experiments. With it he determined the specific heats of calcium, indium, ruthenium, and zinc, using about one gram of material in each case.

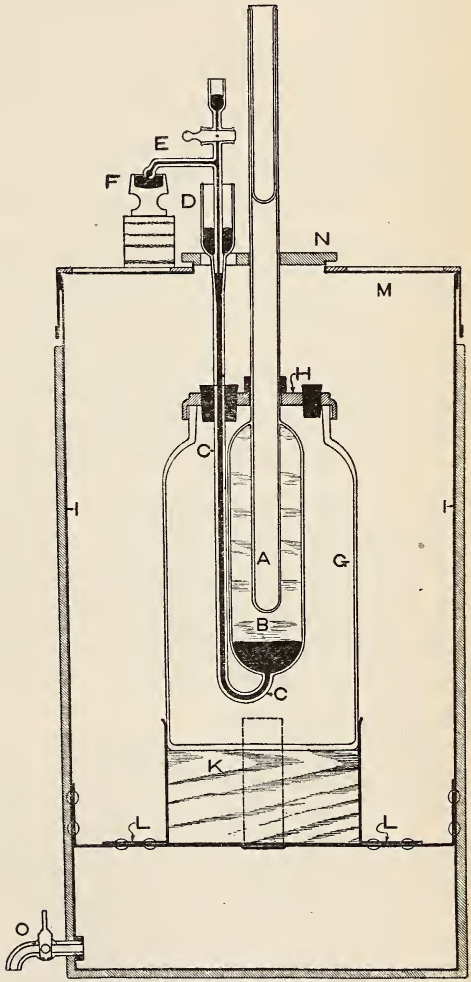

FIG. 1.—The ice calorimeter and ice jacket in vertical section.

Two modifications have been used in the present instrument. The first is the substitution of the reading arm, E (see fig. 1), for the capillary tube, which showed directly the contraction of the contents of the calorimeter. This reading arm[1] consists of an extension of the arm C by which it is possible to establish and interrupt connection between the mercury in the calorimeter and that in a vessel, F, suitable for weighing. The vessel of mercury is weighed, and then connection between the mercury in the vessel and that in the calorimeter is established

[1] First described by Schuller and Wartha in 1877. Schuller, A., and Wartha, V. Calorimetrische Untersuchungen. Wied. Ann. II, pp. 359-383. 1877.

through the small opening in the tip of the arm E. After a certain interval of time this cup is removed and weighed again. The loss of weight tells the amount of mercury which the melting of the ice caused to be drawn into the calorimeter from the cup. In these determinations two cups were used, one of which was attached to the instrument while the other was being weighed. The cups were changed every 5 or 10 minutes during the course of each experiment.

The second modification was necessitated by the use of lake ice instead of newly fallen snow for maintaining the calorimeter at the freezing point. It consists in suspending the calorimeter in an empty glass jar, the air in which affords good insulation between the calorimeter and the ice in which the jar is packed. The idea is due to Boys.[1] The jar is provided with a vulcanite cover, H, which has holes to accommodate the central tube and the side arm. Suspension is effected by wrapping electrician's friction tape tightly around the central tube after passing it through this cover. A rubber stopper with a suitable hole is split and placed around the side arm to close the opening through which the arm passes. The jar is placed in an asbestos-covered galvanized-iron ice can, I, upon a block of wood, K, resting in a rack, L, near the bottom of the can. The metal cover, M, of the can has four holes through which the ice may be replenished These may be opened or closed by revolving a circular piece of linoleum as shown in Plate I. The metal cover is also cut away in the center and a vulcanite cover, N, fitted into the opening. Cover N has suitable holes to permit the passage of the central tube and the side arm of the calorimeter. The ice in the can may, if desired, be replenished by removing the arm E and the metal cap M instead of by simply revolving the linoleum. The can is provided with a cock, O, for draining off water.

Before starting the experiments the calorimeter was thoroughly cleaned and cautiously filled with carefully prepared water of high purity and with freshly distilled mercury. To start the formation of ice, the calorimeter was immersed in a freezing mixture. In this way frondlike crystals were formed through the whole body of water. These were melted almost completely away and the water was then frozen again by evaporating ether in the central tube. The ice so formed was vitreous, developing a tubercular structure on thawing. Ether was used to renew the ice in the calorimeter from time to time

The flow of mercury between the calorimeter and the weighed cup was noted for a sufficient period before and after each run to furnish a correction for heat lost or gained from sources other than the heated wood.

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[1] Boys, C. V. On an addition to Bunsen's ice calorimeter. Phil. Mag. 5 ser. XXIV, pp. 214–217. 1887.

INTERPRETING THE INDICATIONS.

In order to interpret the changes in weight observed, it is necessary to know the weight of mercury drawn in the calorimeter when one calorie of heat is introduced. This amount can be calculated directly from physical data, and can also be determined experimentally. The method of calculation from physical data was pointed out by Bunsen, and is extremely simple. Let W be the weight in grams of mercury drawn in for one calorie: then

$$W = \left(\frac{V_i - V_w}{H}\right) D_m;$$

where V_i is the specific volume of ice, V_w is the specific volume of water, D_m is the density of mercury, and H is the latent heat of fusion of ice, all at 0° C.

But, since neither V_i nor H is known with sufficient accuracy, this calculation fails to give reliable results. Bunsen[1] actually calibrated his calorimeter by introducing a definite weight of water at 100° C. and noting the change which resulted. He then determined V_i in a separate experiment, and used the formula to calculate H. He found that the introduction of one mean calorie caused a contraction of 0.001133 cubic centimeter, which is the volume occupied by 15.41 milligrams of mercury.

Schuller and Wartha[2] repeated this calibration, using the same method: They found, as the mean of five very concordant results, that the introduction of one mean calorie caused the inflow of 15.442 milligrams of mercury. An accuracy greater than one-tenth of 1 per cent is claimed for this value, and it is generally recognized as the most reliable that has been secured. Velten[3] found 15.47 for this value.

Dieterici[4] accepted the value obtained by Schuller and Wartha, after discarding the last place as insignificant, and pointed out that it was the mean of the values obtained by Bunsen and by Velten. He accepted and used this result without checking it.

Von Than,[5] Nessen,[6] and Chappuis[7] contributed nothing to the knowledge of this factor. Mond, Ramsay, and Shields[8] followed

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[1] Bunsen, R.; l. c.

[2] Schuller, A., and Wartha, V. Calorimetrische Untersuchungen. Wied, Ann. II, pp. 359–393. 1877.

[3] Velten, A. W. Das specifische Wärme des Wassers. Wied. Ann. XXI, 31–64. 1884.

[4] Dieterici, C. Ueber eine Bestimmung des mechanischen Aequivalentes der Wärme und über die specifische Wärme des Wassers. Wied. Ann. XXXIII, pp. 417–444. 1888.

[5] V. Than, C. Die Verbrennungswärme des Knallgases in geschlossenen Gefässen. X, Ber. d. deutschen chem. Gesellschaft, pp. 947, 952. 1877. Thermoschemische Untersuchungen. Wied. Ann. XIII, pp. 84–105. 1881.

[6] Nessen, F. Ueber die specifische Wärme des Wassers. Wied. Ann. XVIII, pp. 369–386. 1883.

[7] Chappuis, J. Sur les chaleurs latentes de vaporisation de qulques substances très volatiles. Ann. de Chem. et Phys. 6 ser. XV, pp. 498–517. 1888.

[8] Mond, L., Ramsay, W., und Shields, J. Ueber die Okklusion von Sauerstoff und Wasserstoff durch Platinschwarz. II. Zeitsch. für Phys. Chemie, XXV, pp. 657–685. 1898.

Dieterici, but checked the value by determining the specific heats of lead and zinc.

The factor 15.44 was used in the present work. This value was checked at the end of the work by determining the heat of neutralization of hydrochloric acid with sodium hydroxide. (See Appendix.)

THE BALANCE.

A Spoerhase analytical balance (see Plate I), sensitive to one-fiftieth of a milligram, and a set of first-quality Sartorius weights, were used in all determinations of weight, but fractions of a milligram were disregarded in the regular series of weighings.

In weighing the cups of mercury a counterpoise was used to avoid wear of the larger weights. This counterpoise was a cup half filled with mercury and covered with a plate of glass sealed on with Canada balsam. Inasmuch as differences in the weight of the cups were alone significant, the weight of this counterpoise was not determined.

WEIGHT, TEMPERATURE, AND VOLUME DETERMINATIONS.

The green or air-dry cylinders were first brought to the oven-dry condition by being placed in the oven at about 105° centigrade for about two days and then weighed at intervals until their weight became constant to within 1 milligram for eight hours. This constant weight was recorded in each case as the oven-dry weight of the specimen. The cylinder, before being weighed, was cooled in a stoppered test tube and then transferred to a vessel of known weight in which it was placed on the balance pan.

The oven-dry cylinder was brought to an even temperature all through by being held in the oven for at least 18 hours after the oven-dry condition had been reached, during the last half hour of which the temperature of the oven was kept constant to within one-tenth of a degree centigrade. The bulb of the thermometer was within a centimeter of the cylinder to be used in the ensuing run.

The transfer from the oven to the calorimeter was made in a pair of silvered Dewar tubes. The cylinder was placed in the smaller tube, fitting it loosely, and the smaller tube inserted, mouth first, into the larger one. These tubes were kept in the oven except when in use and always had the same temperature as the wood they carried.

At the end of the experiments the densities of all cylinders were found by measuring their volumes through the displacement of mercury in a graduated cylinder. This method failed only with red oak, into the vessels of which the mercury entered.

SELECTION AND PREPARATION OF THE WOOD.

The wood was taken from material on hand at the Forest Products Laboratory, and was selected to reveal variations in the specific heat of oven-dry wood due to three causes: (*a*) Position of the wood in the bole of the tree; (*b*) locality and site where grown; (*c*) species. The native species were botanically identified; of the four foreign species, two came with the names given. The species are as follows:

White pine..............*Pinus strobus* L.
Longleaf pine............*Pinus palustris* Mill.
Red spruce..............*Picea rubens* Sargent.
Western hemlock.........*Tsuga heterophylla* (Raf.) Sargent.
Douglas fir..............*Pseudotsuga taxifolia* (Lam.) Britt.
Red cedar................*Juniperus virginiana* L.
Mockernut hickory........*Hicoria alba* (L.) Britt.
Quaking aspen...........*Populus tremuloides* Michx.
Beech....................*Fagus atropunicea* (Marsh.) Sudworth.
Chestnut.................*Castanea dentata* (Marsh.) Borkh.
White oak................*Quercus alba* L.
Red oak..................*Quercus rubra* L.
White elm................*Ulmus americana* L.
Sugar maple..............*Acer saccharum* Marsh.
Black gum................*Nyssa sylvatica* Marsh.
White ash................*Fraxinus americana* L.
Unknown wood, foreign, very light.
Mai champah from Siam. *Michelia.*
Unknown wood, foreign, heavier than water.
Cocobola negra from Costa Rica. *Lecythis costaricensis* Pittier.

The 16 indigenous species were chosen to include various forms of nonporous, ring-porous, and diffuse-porous woods. Their density varied from that of white pine to that of hickory. The four foreign woods were selected on account of their high or low density.

The great majority of the native woods were taken from short logs from the bole of the tree, usually from somewhere near breasthigh. Cylinders were cut in such a way that their axes ran with the grain of the wood and were turned on a lathe. Each cylinder was about 17 millimeters in diameter and 3 to 9 centimeters long, the length depending upon the weight, which was preferably about 6 grams. Each cylinder was marked with an Arabic numeral to indicate the species and the log from which it was taken and also with a capital letter to distinguish it from other cylinders cut from the same piece.

To learn the variation due to the position of the wood within the bole of the tree and to the locality and site where the wood was grown a single species was selected. Douglas fir was chosen because of its wide range both geographically and ecologically and because of the great difference in quality shown by wood of this species from different localities. Sticks collected by members of the Forest

Service in three different parts of its range and two sticks from different sources purchased in Madison, Wis., were used. The material showed a variation of from 3 to 20 rings per centimeter and a difference in density of from 0.40 to 0.59. A piece was cut from just above the stump and another from the bole near the crown, and from each of these pieces cylinders were made representing successive positions between the pith and the bark. No branch wood was studied. When the many determinations on Douglas fir showed no consistent variation of specific heat due either to the position of the wood in the bole or to the place where the tree grew it seemed fairly certain that no such variation existed in any species. Nevertheless, three sticks each of red oak and sugar maple were secured from widely separated localities and possibly from different though closely related species. For these, likewise, no difference in specific heat could be detected within the species. Therefore, when the study of other woods was taken up no attention was paid to the part of the tree from which the cylinders were taken or to the locality whence the wood came.

RESULTS.

The chief results of this work are two: First, the mean specific heats of 20 species of wood have been accurately measured over the interval between 106° C. and 0° C.; second, preliminary results have been secured which indicate a great variation of specific heat with temperature. Also an increase of specific heat was encountered which was apparently due to steaming.

MEAN SPECIFIC HEAT.

A summary of the determinations of the mean specific heat for each species is given in Table 1, in which the values corrected by the frequency curve (see appendix) are shown in the last column. Results (calculated) for each cylinder of wood are given in Table 5, appendix.

TABLE 1.—*Specific heat of oven-dry wood—averages by species.*

Species.	Number of determinations.[1]	Density.	Mean specific heat 106°–0° C.	
			Calculated from observations.	Corrected.[2]
Douglas fir	37	0.48	0.325	0.327
Longleaf pine	2	.68	.335	.337
White pine	2	.25	.329	.331
Western hemlock	2	.45	.320	.322
Red spruce	2	.39	.330	.332
Red cedar	2	.46	.322	.324
Red oak	13	.62	.329	.331
White oak	3	.78	.323	.325
Chestnut	4	.32	.315	.317
White elm	2	.64	.323	.325
Mockernut hickory	2	.84	.325	.327
White ash	3	.63	.325	.327
Sugar maple	12	.66	.325	.327
Quaking aspen	2	.42	.327	.329
Beech	2	.75	.324	.326
Black gum	2	.52	.323	.325
Cocobola negra from Costa Rica	2	.92	.325	.327
Mai champah from Siam	2	.32	.321	.323
First unknown wood	2	1.10	.322	.324
Second unknown wood	2	.23	.320	.322

[1] For the rejection of 16 determinations see appendix.
[2] The determination of the correction is discussed in the appendix.

The average of the calculated values for the specific heat of wood obtained by giving equal weight to each of the 20 species studied is 0.3244; that obtained by giving equal weight to each of the 100 runs shown in Table 1 is 0.3249. The close agreement between these averages, in spite of the fact that one-half of the runs was made upon Douglas fir and maple, shows strikingly how little influence species has upon the specific heat of wood. The average referred to hereafter, unless otherwise specified, will be that giving equal height to each of the 100 runs 0.325 calculated, or 0.327 corrected.

The table shows the specific heat of longleaf pine to be about 3 per cent greater than the average, and that of chestnut to be the same amount less. But the values for these species are the mean of only a few results, and are therefore much less reliable than the average with which they are compared. A consideration of the probable error of the observations indicates that this difference must be at least 4 per cent to acquire significance. The differences shown in the table may be real, but are too small to be significant, and furnish no basis for drawing a distinction between the specific heat of different species or of conifers and broadleaf trees. Therefore, the mean specific heat of oven-dry wood may be considered 0.327, and this figure remains nearly constant for all wood.

EFFECT OF LOCALITY.

The variation in specific heat within a species due to the locality in which it is grown was so small and inconsistent as to furnish no basis for concluding that locality influences the specific heat of

wood. The values obtained by the experiments along this line are given in Table 2:

TABLE 2.—*Results of determinations on the same species of wood grown in different localities.*

Species.	Source.	Stick.	Mean specific heat 106°–0° C.	Number of determinations.
Douglas fir	Commercial	5	0.3248	9
	Portland, Oreg	6	.3286	2
	Commercial	7	.3288	2
	Denver, Colo	8	.3232	5
	Snoqualmie National Forest	9	.3282	4
		10	.3277	12
Sugar maple	Glandon, Wis	11	.3242	4
	do	12	.3264	4
	Corbin Park, N. H	14	.3250	4
Red oak	Richland Parish, La	15	.3320	4
	Glandon, Wis	18	.3298	4
	Brandywine, Md	19	.3286	4

HEARTWOOD AND SAPWOOD.

The differences met in cylinders taken from the heartwood and sapwood on a line passing from the pith of a tree to the bark are even smaller than the differences in a species grown in different localities. The results are given in Table 3:

TABLE 3.—*Results of determinations on heartwood and sapwood of Douglas fir.*

Material.	Cylinder.	Mean specific heat 106°–0° C.
Heartwood	10D	0.3258
	10F	.3260
	10H	.3260
Sapwood	10J	.3259
	10L	.3262

CORRECTED RESULTS.

The above results were generalized by means of a frequency curve. (Appendix, p. 21.) This curve revealed the fact that the results are subject to a systematic error which tends to make the average result of 0.325 too low by about five-tenths of 1 per cent. This error, there is no reason to doubt, has its origin in the loss of heat during the transfer of the specimen from the oven to the calorimeter. Applying this correction gives a corrected value of 0.327, which is the most acceptable result for the mean specific heat of oven-dry wood through the interval between 106° C. and 0° C., and is believed to be correct within six-tenths of 1 per cent.

The two following rules may be laid down for the practical use of these results:

1. When the particular species, the specific heat of which is desired, is one of the eighteen named in Table 1, use the corrected value given in the last column of the table.

2. When the particular species is not given in Table 1, or is unknown, or when the wood of more than one species is lumped together in unknown proportions, use the value 0.327.

VARIATION IN SPECIFIC HEAT WITH TEMPERATURE.

In determining the variation in specific heat with temperature, the mean specific heat between 106° C. and 0° C. was taken as one point. Runs were made from approximately 65° and 25° to determine the mean specific heats between each of these temperatures and 0° C. A larger number of intervals will be necessary before the shape of a curve showing the variation in specific heat with temperature is known. The present results can be considered as only preliminary because the peculiar precautions taken to keep the wood in an oven-dry condition at these temperatures introduced errors which were not entirely removed by correction. The results are given in Table 4.

TABLE 4.—*Results of determinations with different initial temperatures.*

Run.	Cylinder.	Initial temperature.	Mean specific heat.
75	14C	109.40	0.314
76	19D	109.05	.326
124	18B	23.20	.280
125	19D	23.20	.280
126	14C	23.10	.281
132	14C	62.95	.299
133	18B	63.85	.286
134	19D	63.35	.286
136	22A	68.05	.297
137	25B	68.45	.295
139	18B	67.00	.289
140	19D	66.50	.286

The highest values obtained for each temperature are the most probable. Even these indicate an unusually large variation of specific heat with temperature.

By plotting the values for the two lower temperatures shown in the table and that for 106° C. already obtained, it was found that the specific heat of wood falls to the neighborhood of 0.266 at 0° C. Therefore, when represented by a straight-line formula, the value of the true specific heat at temperature t is indicated by the following equation:

$$\text{Specific heat} = 0.266 + 0.00116t$$

The mean specific heat through any interval of temperature is, under this assumption, of course equal to the true specific heat at the mean temperature. The values given are subject to correction when a large number of runs from different temperatures have been made. They are advanced at the present time merely to set forth the best knowledge at hand.

EFFECT OF STEAMING ON SPECIFIC HEAT.

The wood used in five runs, Nos. 47, 48, 49, 50, and 51, was placed in the oven at 110° C. while still moist, and dried in nearly saturated air at this temperature. Of these five pieces of wood three showed a greatly increased specific heat. Accordingly it appears possible that exposure to moisture at high temperature increases the specific heat of wood. If this is true, other properties, and with them technological characters, may also change. This behavior needs further study.

APPENDIX.

THE CALIBRATION OF THE CALORIMETER.

The value 15.44 milligrams for the weight of mercury drawn into the calorimeter by the introduction of one calorie of heat was checked by measuring the heat of reaction of hydrochloric acid and sodium hydroxide. The advantage of this method of calibration is that it avoids all measurements of temperature and all error due to loss of heat in dropping a hot body down the tube of the calorimeter.

Half-normal solutions were used. The acid was carefully prepared and standardized, both against solutions of known strength and by determining the chlorine as silver chloride. Ten cubic centimeters were used. The alkali was prepared with less care and used in excess, the use of the ice calorimeter requiring that but one reagent be present in known amount and high purity. The weight of mercury drawn in in three runs was 1.1731, 1.1729, and 1.1725 grams; the average being 1.1728 grams. For the solution used (0.5078 normal) this gave 14,958 for the heat of neutralization.

Such calibration is not entirely satisfactory because this value has been determined before only at higher temperatures and the specific heats of dilute solutions are not known with sufficient accuracy to permit the calculation from one temperature to another. Julius Thomsen[1] has studied the change of heat of neutralization with temperature and gives values for this reaction at 25° C. and 10° C. The value obtained appears high when compared with these two, but it is to be noted that the accepted value for this heat of reaction at 18° is low by the same comparison. In fact, the three values for 18°, 10°, and 0° C. lie nearly in a straight line. It is hoped that the heat of this reaction at zero will be accurately determined by other methods and so remove the only objection to the use of this excellent method of calibration.

PROCEDURE IN GENERALIZING RESULTS.

Upon completion of the measurements and calculation of the results it becomes necessary to determine the best representative value and to measure the consistency of the results, and, on the basis of this measure, to form an estimate of the reliability of the representative value determined. Accurate results are always discordant,

[1] Thermochemische Untersuchungen. Bd. I, p. 64.

due to chance errors which are unavoidable; in addition they may be biased by the presence of systematic errors. Chance errors obey certain mathematical laws which have been formulated by Laplace; their measure is obtained by purely mathematical processes and consists either of the mean error or the "probable" error. Systematic errors are susceptible of no mathematical treatment, and, unless they are very simple, their discussion leads to no numerical corrections. Their presence is best revealed by the form of the frequency curve and its relation to the arithmetic mean.

REJECTED RESULTS.

In Table 5 are displayed the material used in each of the 116 runs made from near 106° C., the number and date of each run, the corrected observations, and the calculated results. The records of each one of these runs were carefully scrutinized, and where there was valid reason for doubting the fitness of any result it was rejected. Rejections were made for two reasons:

1. In the preparation of some of the material the wood was exposed to temperatures of 110° C. while still wet and dried in nearly saturated air at this temperature. Such treatment darkened the color of the wood, produced abnormal shrinkage, and, in some cases, appeared to raise its specific heat. To avoid the possible effects of such drastic treatment the results from the five runs, Nos. 47, 48, 49, 50, and 51, for which such material was used, were rejected entirely and a notation to that effect entered in the column headed "Remarks."

2. While nearly all of the runs were made from an initial temperature between 102° and 112° C., three runs, Nos. 23, 24, and 25, were made from temperatures above 120° C. The departures of these runs from the average of the remaining results is not sufficiently consistent to warrant their rejection; but inasmuch as there are indications that the specific heat of wood varies greatly with temperature, the results of these three runs are also rejected.

The arithmetical mean of the remaining results was now calculated as a first approximation to the best representative value, and the criterion of permissible discordance was applied to the individual results. One of the practical rules resulting from the laws governing the behavior of chance errors is, that if *one* result of a series differs from the average of the *other* results by an amount which is more than four times the average deviation of the other results, the discordant result should be rejected, because to include it lowers the reliability of the average. If, in the application of this rule, the doubtful result is included in the average, the permissible discordance is increased and the criterion made looser. Obviously any result whose rejection is indicated under this application would certainly be

rejected if the rule were followed strictly. The advantage of applying the rule in this way is that under it more than one result may be rejected at a time.

After the omission of the eight runs already rejected, 108 results are left for further consideration. Their average is 0.320, and their mean discordance ±0.011; so that all results greater than 0.364 and less than 0.276 are properly rejected. This includes four runs, Nos. 4, 16, 22, and 26, and leaves 104 results to which the same criterion is again applied. The average is now raised to 0.324, and the average discordance reduced to 0.006, so that results greater than 0.348 and less than 0.300 are properly rejected. Again, the results of four runs, Nos. 2, 81, 93, and 100, are marked for rejection and an even hundred results remain. Their mean value is 0.32486, their mean discordance 0.00518, and only results above 0.345 and below 0.304 can be rejected. None falls outside these limits. It is noteworthy that every one of the eight results rejected in the two successive applications of this criterion fell below those retained. The reason why all the faulty results were low and none were high will be shown later in discussing the reliability of the average in the light of the frequency curve.

The 100 results finally indicated for retention are now searched for systematic variation demanding corrections. The most obvious correction to apply would be for the varying temperatures at which the wood entered the calorimeter. Accordingly the results are tested for variation with initial temperature. This is done graphically, as shown in figure 2, which is made by plotting the individual results, giving each an abscissa determined by its temperature and an ordinate determined by its specific heat. The result is to scatter the points over the paper with seemingly no well-marked trend. But the trend is more clearly revealed when the results for successive intervals of temperature, such as half degrees, are averaged, as shown in the figure. These averages vary considerably, their range extending from 0.321 to 0.330, but the course of the line joining them is generally horizontal. Should any correction be decided upon, it would be an inverse function of temperature, which is the opposite of what results at lower temperatures indicate and would be small. Therefore a correction for temperature appears unwarranted.

Possible variation with species, density, etc., have already been disproven.

FREQUENCY CURVE.

The next step is the construction of the frequency curve shown in figures 3 and 5; figure 3 shows the development of this curve. The results of the separate runs were first arranged in order of magnitude, beginning with the smallest, 0.308, and ending with the largest,

0.340. Between these extremes is a difference of 32 units in the third decimal. It is convenient, then, to group the results into 32 classes, those lying between 0.308 and 0.309 forming Class A; those between 0.309 and 0.310 forming Class B, etc. Convenience is the only reason for making 32 classes. Forty or 20 or 25 might as correctly have been formed. Fifty would have been too many, as there would be an average of but two results in each class. Five would have been too few, not because 20 results in each class are too many but because five points would not show all the properties of the curve. The number of results in each one of the 32 classes formed is shown by the ordinates of the successive points on the lowest of the broken

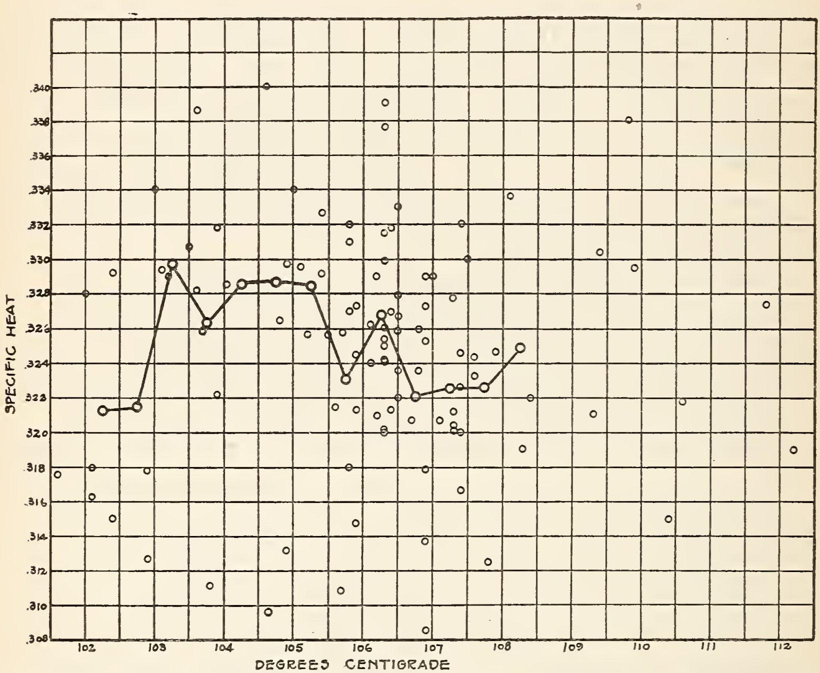

FIG. 2.—Distribution of results through range of initial temperatures, and average results for each half degree.

lines in figure 3. The sum of the ordinates under this line is 100. The variations in the successive ordinates indicate that the classes have been made too small. The pairing of successive classes AB, BC, CD, etc., and taking the number of observations in each pair, gives the second broken line in which, although the variation of successive ordinates has been reduced considerably, still further reduction appears advisable. For this purpose successive classes are united in threes, thus ABC, BCD, CDE, etc. When the number of results in each group of three is plotted, the successive frequencies show a much smaller irregular variation, as indicated in the upper broken

line in figure 3. By continuing to form successively larger groups smoother and smoother lines can be obtained, but it is better to make further adjustment in another way, leaving the work just performed with the decision to use groups of three successive classes in plotting the final curve.

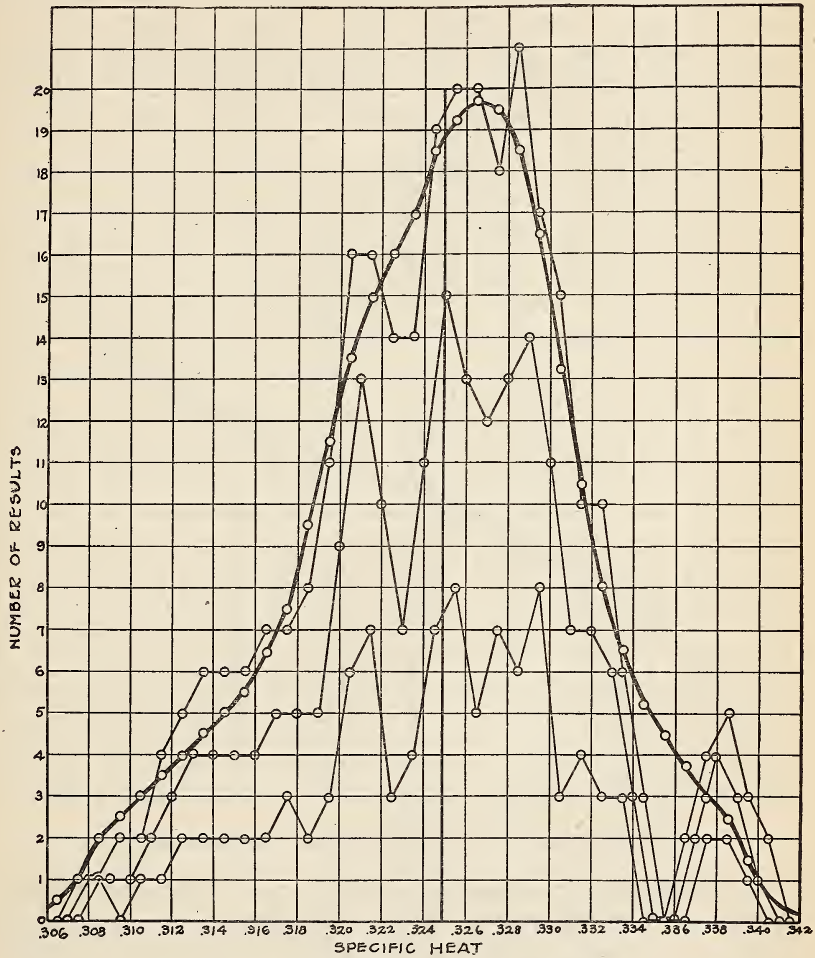

FIG. 3.—Frequency curve and its development.

The essential feature of the preceding method of grouping is the application of a correction to the number of results in each class according to the number of results in the two adjacent classes. Of course the graphical method of rounding off the results immediately suggests itself, and is used in the distribution curve, figure 4. The ordinates indicate specific heats and the abscissas the number of results. The individual results, arranged in order of their magnitude, are placed at equal distances apart along the horizontal axis; and each is

given the ordinate indicated by its magnitude. Connecting these in order gives an irregular broken line. But a regular curve, whose form approaches that of the cubical parabola ($a^2y=x^3$), can be so drawn as to pass through many of the individual results and very close to the remainder. The abscissa intercepted by this curve at any ordinate indicates the corrected number of results below the value of the ordinate taken. The corrected number of results in each class (ABC, BCD, CDE, etc.) can thus be obtained from the curve. This distribution differs from the observed by the amount which the curve departs from the points plotted. The cor-

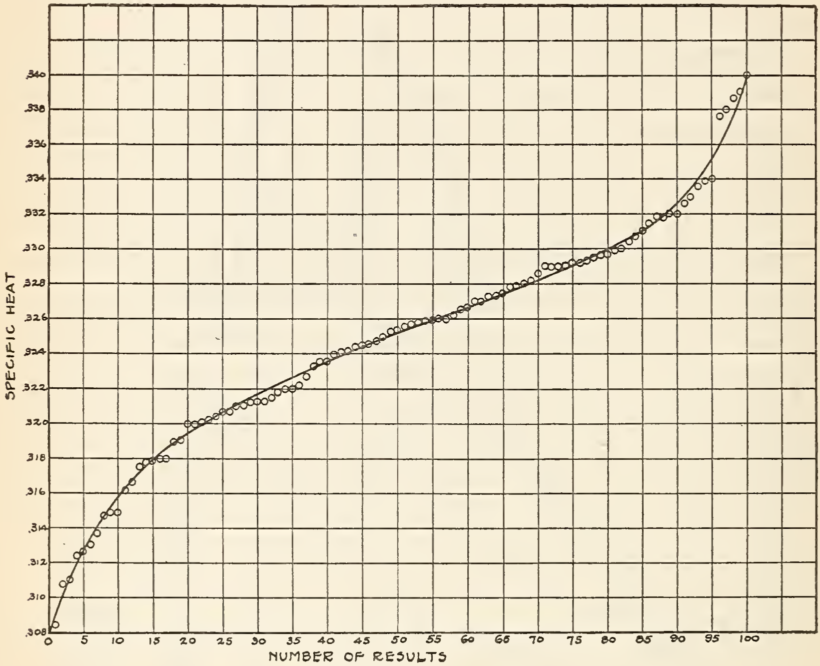

FIG. 4.—Curve for correcting distribution of results for a smooth frequency curve.

rected distribution, read from this curve, is nearer the truth than the observed distribution because the irregularities in the observed distribution are unnatural and would disappear if the number of points were greater.

The frequency curve shown in figures 3 and 5 is obtained from the corrected distribution of results derived from figure 4. It is entered on figure 3 merely to show its relation to the broken lines indicating the distribution of the results actually observed and is repeated on figure 5 for further discussion. This curve furnishes the best information which can be secured regarding the reliability of the mean value of the specific heat of wood.

This frequency curve is not a regular curve, though its grosser irregularities have been removed and its essential characteristics more clearly revealed. The irregularities left are best revealed by a comparison with the true frequency curve, $y = e - x^2$, shown in figure 5. The proportions of the true curve are obtained by giving it the same height and the same modulus as the curve under discussion.

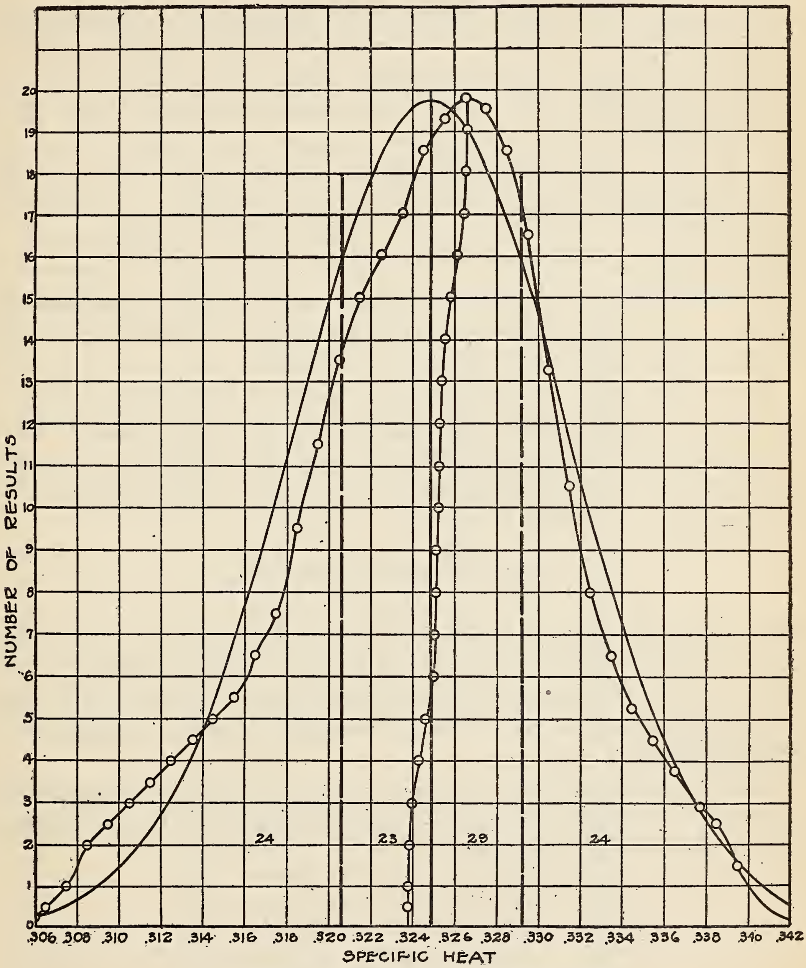

FIG. 5.—Empirical and theoretical frequency curves.

Its apex is placed on the ordinate of the average of the observed results. The comparison shows two ways in which the curves differ: (1) the empirical curve is too broad below; and (2) its crest is bent to the right toward the higher values of the specific heat. This inclination is clearly shown by the course of the median line of the empirical curve and its deviation from the median line of the true or

theoretical frequency curve which is formed by the ordinate over the average specific heat. The way in which the empirical curve differs from the true curve indicates the presence of a systematic error which tends to make the individual results too low by a varying amount. It was the exaggerated prominence of this error which led to the rejection of the results of eight runs under the procedure followed on page 20.

The nature of the error is learned by reviewing the apparatus and methods employed. There is no reason to doubt that its origin lies in the loss of heat during the transfer of the specimen from the oven to the calorimeter. In other words, the assumption made in all calculations that the hot specimen reached the interior of the calorimeter at the same temperature as that indicated by the thermometer in the oven before its removal is not entirely justified. The effect of this error is to make the average 0.325 too low; judging from an inspection of the curve the true value lies near 0.327. The error in the result 0.325 due to this systematic error is about one-half of 1 per cent, and the corrected value 0.327 contains a residual systematic error of about the same magnitude or smaller.

The chance error of the result is readily calculated according to the theory of probability. The probable error of a single result is obtained by the following formula, in which d is the amount by which each individual result differs from the average of the results, and n is the number of results averaged:

$$\text{probable error} = 0.67\sqrt{\frac{\Sigma d^2}{n-1}}.$$

This calculation gives 1.3 per cent for the probable error of a single result. The probable error of the average varies inversely as the square root of the number of results averaged. Thus for the average of 100 results the probable error is one-tenth that for a single result, or one-tenth of 1 per cent.

The sum of the two errors, or six-tenths of 1 per cent, measures the reliability of the result secured for the specific heat of wood between 106° C. and 0° C.; viz, 0.327.

TABLE 5.—*Determinations of the specific heat of wood.*

Species.	Cylinder mark.	Run No.	Date.	Weight of mercury.	Weight of cylinder.	Temperature.	Specific heat.	Remarks.
			1911.	*Mg.*	*Grams.*	°*C.*		
Douglas fir	1 A	26	Jan. 14	4,781	11.238	107.9	0.2552	Rejected in generalizing results. (See appendix.)
Do.	1 A	27	Jan. 17	5,908	11.238	107.4	.3167	
Do.	1 B	24	Jan. 13	6,928	10.988	123.9	.3293	Rejected in generalizing results; high initial temperature.
			1910.					
Do.	1 B	15	Dec. 22	5,486	10.988	103.8	.3112	
Do.	2 A	2	Nov. 1	7,033	14.757	104.9	.2940	Rejected in generalizing results. (See appendix.)
			1911.					
Do.	2 A	21	Jan. 6	7,337	14.757	102.9	.3127	
Do.	2 B	22	Jan. 7	3,072	12.349	102.0	.1580	Do.
Do.	2 B	23	Jan. 13	7,800	12.349	120.2	.3404	Rejected in generalizing results; high initial temperature.
			1910.					
Do.	2 B	16	Dec. 23	4,733	12.349	103.4	.2401	Rejected in generalizing results. (See appendix.)
Western hemlock	3 A	3	Nov. 1	5,935	11.763	102.9	.3178	
Do.	4 A	1	Oct. 31	5,000	9.510	105.9	.3213	
Douglas fir	5 A	4	Nov. 14	4,836	10.863	106.9	.2698	Do.
Do.	5 A	14	Dec. 22	5,661	10.807	103.1	.3294	
Do.	5 B	6	Dec. 7	5,442	10.312	103.5	.3307	
Do.	5 C	7	Dec. 8	5,154	10.355	101.6	.3176	
Do.	5 D	8	...do.....	5,113	9.826	102.4	.3292	
Do.	5 E	9	...do.....	5,458	10.566	102.0	.3280	
Do.	5 F	10	Dec. 9	5,000	10.030	102.1	.3163	
Do.	5 G	11	Dec. 13	4,548	9.126	102.4	.3150	
Do.	5 H	12	...do....	5,382	10.747	102.1	.3180	
Do.	5 I	5	Dec. 1	4,679	8.757	105.1	.3296	
Do.	5 I	13	Dec. 22	4,623	8.713	103.0	.3339	
			1911.					
Do.	6 A	19	Jan. 6	7,354	14.017	103.6	.3282	
Do.	6 B	20	...do....	6,377	12.167	103.2	.3290	
Do.	7 A	17	Jan. 3	5,111	9.793	103.7	.3259	
Do.	7 B	18	Jan. 5	5,460	10.263	103.9	.3318	
Do.	8 A	37	Jan. 24	6,359	11.744	106.3	.3299	
Do.	8 B	38	...do.....	6,861	12.628	107.0	.3290	
Do.	8 E	30	Jan. 18	6,245	12.014	107.8	.3125	
Do.	8 G	29	...do.....	6,424	12.102	107.3	.3204	
Do.	8 H	28	...do.....	6,109	11.345	107.6	.3244	
Do.	9 E	33	Jan. 20	6,079	11.040	107.4	.3320	
Do.	9 F	32	Jan. 19	5,953	11.163	108.3	.3191	
Do.	9 J	31	...do.....	6,711	12.062	108.1	.3336	
Do.	9 K	25	Jan. 13	6,328	10.807	124.0	.3059	Rejected in generalizing results; high initial temperature.
Do.	10 A	34	Jan. 20	5,241	9.461	106.3	.3376	
Do.	10 B	35	...do.....	5,271	9.767	106.2	.3290	
Do.	10 C	36	Jan. 21	5,385	9.822	104.6	.3400	
Do.	10 D	103	Apr. 22	2,684	5.044	105.7	.3258	
Do.	10 E	104	...do.....	3,194	5.979	106.3	.3254	
Do.	10 F	105	Apr. 24	3,080	5.760	106.3	.3260	
Do.	10 G	106	...do....	3,388	6.346	106.8	.3236	
Do.	10 H	107	...do....	3,654	6.795	106.8	.3260	
Do.	10 I	108	Apr. 25	3,182	6.022	106.7	.3207	
Do.	10 J	109	...do.....	3,568	6.656	106.5	.3259	
Do.	10 K	110	...do.....	2,917	5.435	106.5	.3267	
Do.	10 L	111	...do.....	3,776	7.066	106.1	.3262	
Sugar maple	11 A	39	Mar. 8	6,285	11.415	110.6	.3218	
Do.	11 B	40	...do.....	6,332	11.322	109.9	.3295	
Do.	11 C	41	Mar. 9	6,335	11.347	109.4	.3304	
Do.	11 D	43	...do.....	5,937	11.055	110.4	.3150	
Do.	12 A	42	...do.....	7,524	13.885	109.3	.3211	
Do.	12 B	44	Mar. 10	7,005	12.220	109.8	.3380	
Do.	12 C	45	Mar. 11	6,631	12.001	112.2	.3190	
Do.	12 D	46	...do.....	6,665	11.795	111.8	.3274	
Do.	13 A	47	Mar. 17	7,298	12.972	104.5	.3486	Rejected in generalizing results. Steamed wood used.
Do.	13 B	48	Mar. 18	7,216	13.000	104.4	.3441	Do.
Do.	14 A	52	Mar. 24	6,748	12.469	107.9	.3247	
Do.	14 B	53	...do.....	7,202	13.269	107.3	.3278	
Do.	14 C	54	...do.....	6,541	12.154	107.4	.3246	
Do.	14 D	55	...do.....	6,719	12.561	107.4	.3227	

TABLE 5.—*Determinations of the specific heat of wood*—Continued.

Species.	Cylinder mark.	Run No.	Date.	Weight of mercury.	Weight of cylinder.	Temperature.	Specific heat.	Remarks.
			1911.	*Mg.*	*Grams.*	° *C.*		
Red oak	15 A	56	Mar. 27	5,986	11.061	103.6	.3386	
Do.	15 B	57	...do.....	6,165	11.692	104.1	.3286	
Do.	15 C	59	Mar. 28	5,907	10.915	105.0	.3340	
Do.	15 D	58	Mar. 27	5,697	10.666	105.8	.3270	
Do.	16 A	50	Mar. 22	5,175	10.333	105.1	.3090	Rejected in generalizing results. Steamed wood used.
Do.	17 A	49	Mar. 18	6,062	11.331	104.5	.3317	Do.
Do.	18 A	60	Mar. 28	6,484	12.089	105.4	.3292	
Do.	18 B	61	...do.....	6,070	11.220	105.8	.3310	
Do.	18 C	62	...do.....	6,283	11.894	104.8	.3265	
Do.	18 D	63	Mar. 29	6,385	11.800	105.4	.3326	
Do.	19 A	64	...do.....	6,747	12.636	104.9	.3297	
Do.	19 B	65	...do.....	6,784	12.828	105.2	.3257	
Do.	19 C	67	Mar. 30	6,274	12.072	105.8	.3180	
Do.	19 C	70	Mar. 31	6,460	12.072	105.9	.3273	
Do.	19 D	69	...do.....	6,481	11.891	106.4	.3318	
Red cedar	21 A	51	Mar. 23	4,958	8.986	104.4	.3423	Do.
Quaking aspen	22 A	66	Mar. 30	4,342	8.403	103.9	.3222	
Do.	22 B	68	Mar. 31	4,309	7.945	105.8	.3320	
Red cedar	23 A	80	Apr. 11	4,580	8.716	106.3	.3202	
Do.	23 B	81	...do.....	2,920	5.909	106.9	.2990	Rejected in generalizing results.
Do.	23 B	82	Apr. 12	3,136	5.909	106.1	.3240	
Longleaf pine	24 A	78	Apr. 11	7,178	12.887	106.3	.3390	
Do.	24 B	79	...do.....	6,816	12.527	106.3	.3315	
White pine	25 A	71	Apr. 6	2,552	4.658	107.5	.3300	
Do.	25 B	72	...do.....	2,696	4.961	106.9	.3290	
Red spruce	26 A	73	...do.....	4,090	7.570	106.9	.3273	
Do.	26 B	74	...do....	4,508	8.230	106.5	.3330	
Beech	27 A	83	Apr. 12	8,090	15.439	105.6	.3215	
Do.	27 B	84	...do.....	7,466	14.086	105.5	.3256	
Chestnut	28 A	85	...do.....	5,617	10.901	105.9	.3148	
Do.	28 A	87	Apr. 13	5,720	10.901	106.9	.3179	
Do.	28 B	86	Apr. 12	4,800	9.460	104.9	.3132	
Do.	28 B	88	Apr. 13	4,901	9.460	106.9	.3138	
White oak	29 A	89	...do.....	7,421	14.562	106.9	.3086	
Do.	29 A	92	Apr. 14	4,904	9.290	106.4	.3213	
Do.	29 B	90	...do.....	5,815	10.931	106.3	.3242	
White elm	40 A	91	...do.....	4,422	8.353	106.5	.3220	
Do.	40 B	93	...do.....	3,832	7.860	106.3	.2970	Do.
Do.	40 B	94	Apr. 18	4,183	7.860	106.3	.3241	
Mockernut hickory	41 A	95	...do.....	6,257	11.648	106.4	.3270	
Do.	41 B	96	...do.....	6,484	12.187	106.5	.3236	
Black gum	42 A	97	Apr. 19	3,860	7.234	106.3	.3250	
Do.	42 B	98	...do.....	3,943	7.497	106.2	.3210	
White ash	43 A	99	...do.....	4,924	9.707	105.7	.3109	
Do.	43 A	100	Apr. 20	4,722	9.707	107.4	.2934	Do.
Do.	43 A	102	Apr. 21	5,230	9.707	106.5	.3279	
Do.	43 B	101	Apr. 20	4,585	8.610	107.3	.3212	
Unknown wood, very light.	44 A	113	Apr. 26	2,506	4.774	106.3	.3200	
	44 B	114	...do.....	2,349	4.429	107.4	.3200	
Mai champah	45 A	117	Apr. 27	3,597	6.668	108.4	.3220	
Do.	45 B	118	...do.....	3,519	6.634	107.1	.3207	
Unknown wood, heavier than water.	46 A	115	Apr. 26	3,637	6.853	107.3	.3201	
	46 B	116	...do.....	3,673	6.839	107.6	.3233	
Cocobola negra	47 A	119	Apr. 27	3,347	6.232	106.9	.3253	
Do.	47 B	112	...do.....	3,303	6.226	105.9	.3245	

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